

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 896 046 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
10.02.1999 Bulletin 1999/06

(51) Int. Cl.⁶: C09K 3/16, D21C 9/00,
D21H 17/72

(21) Application number: 98201485.4

// (D21H17/06, 17:07, 17:14)

(22) Date of filing: 12.05.1998

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

• Eka Chemicals AB
445 80 Bohus (SE)
Designated Contracting States:
FI SE

(30) Priority: 06.08.1997 EP 97850120

(72) Inventors:
• Thebrin, Ingemar
444 41 Stenungsund (SE)
• Ankarbratt, Lisbeth
444 46 Stenungsund (SE)

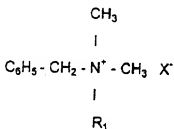
(71) Applicants:
• AKZO NOBEL N.V.
6800 SB Arnhem (NL)
Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE

(74) Representative:
Jönsson, Christer et al
Eka Chemicals AB,
Patent Department,
Box 11556
100 61 Stockholm (SE)

(54) A Composition for treatment of cellulosic material

(57) An aqueous softening and antistatic agent composition comprising a quaternary ammonium compound and a biodegradable nonionic surfactant, which composition comprises a quaternary ammonium compound having the formula

treated with the composition.



wherein R₁ is a C₆ - C₂₂ hydrocarbyl group; and X is halogen or SO₄²⁻, in a concentration of at least about 15% by weight. The surfactant is a linear alkoxylated fatty acid or a linear alkoxylated unsaturated alcohol. Furthermore a method for providing cellulosic materials with a reduced tendency to retain an electrostatic charge as well as providing said material with improved softness, wherein the cellulosic material is treated with said composition, and fluff obtainable from fluff pulp

EP 0 896 046 A1

Description

[0001] The present invention relates to an aqueous softening and antistatic agent composition, which is useful for the treatment of cellulosic material, in particular fluff pulp, fluff, and tissue. Said composition comprises a quaternary ammonium compound and an alkoxylated fatty acid or an alkoxylated fatty alcohol. Furthermore the invention also relates to a method for providing cellulosic materials with a reduced tendency to retain an electrostatic charge as well as providing the material with improved softness, wherein the material is treated with said composition.

[0002] Softening and antistatic agents are frequently used in the production of fluff and tissue.

[0003] EP-A-765,418, for instance, relates to a method for the production of fluff pulp in which an antistatic agent composition comprising quaternary ammonium compounds is used; the composition is however not indicated to have any softening properties.

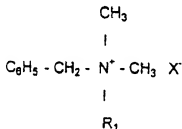
[0004] On the other hand WO 97/04170 discloses a tissue containing a softening composition comprising quaternary ammonium compounds and fatty acid alkoxylate or ethoxylated glycerine or lanolin, which is not indicated to have any antistatic properties.

[0005] US-A-4,476,323, however, discloses a composition which is used in a process for the treatment of cellulosic materials to impart a reduced tendency to retain an electrostatic charge and improved softness and/or reduced mechanical strength due to the reduction in interfiber bonding. The composition contains certain quaternary ammonium compounds which comprises in particular a 2-hydroxy-oxypropylene group, which is believed to provide the combined antistatic and softening properties. Apart from this, the composition may contain nonionic surfactants, such as alkoxylated aliphatic alcohols or acids. There is no suggestion given about the compositions biodegradability.

[0006] US-A-5,312,522 discloses however a biodegradable softening composition used in paper products such as tissue. The composition contains certain quaternary ammonium compounds, namely mono- and diester variations of some common quaternary ammonium salts, which esters are said to be biodegradable, in contrast to the corresponding salts; the esters are also said to function as debonding agents. Optionally, the composition may also contain nonionic surfactants such as alkylpolyethoxylated esters. No indication is given about any antistatic properties of the composition.

[0007] It would be - particularly in view of the documents referred to above - desirable to be able to provide a softening and antistatic agent composition useful for the treatment of cellulosic material, which composition is biodegradable. Thus, the problem to be solved by the present invention is to provide such a composition.

[0008] In view of what is stated in US-A-5,312,522 (referred to above) about the biodegradability of common quaternary ammonium salts, the problem has now surprisingly been solved by the composition defined in appended claim 1. In more detail the present composition is an aqueous softening and antistatic agent composition comprising a biodegradable nonionic surfactant and a quaternary ammonium compound having the formula



wherein R_1 a $\text{C}_8 - \text{C}_{22}$ hydrocarbyl group; and X is halogen or SO_4^{2-} , the concentration of the quaternary ammonium compound in the composition being at least about 15% by weight, preferably at least about 20% by weight. The quaternary ammonium compound may, for instance, be chosen among $\text{C}_{12} - \text{C}_{16}$ alkyl dimethyl-benzylammonium salts and benzylcoco-alkyldimethyl-ammonium salts. In a preferred embodiment of the invention the quaternary ammonium compound is a benzyl-cocoalkyldimethyl-ammonium salt. The anion of the salt may be chosen among the halogen ions, particularly the chloride and bromide ions, and the sulphate ion, although in the preferred case it is a chloride ion; the Chemical Abstracts Service Registry Number of this preferred substance is 61789-71-7. The cocoalkyl group comprises even-numbered, aliphatic, straight-chained $\text{C}_8 - \text{C}_{18}$ hydrocarbyl groups. In a preferred embodiment each one of the $\text{C}_8 - \text{C}_{18}$ hydrocarbyl groups in the cocoalkyl group represents at least about 2 mole-%, calculated on the total number of moles of said hydrocarbyl groups chains in said cocoalkyl group. The preferred mole percentage ranges of the hydrocarbyl groups in the cocoalkyl group are indicated in Table I below

Table I

HYDROCARBYL GROUP	MOLE PERCENTAGE RANGE
C ₈	2-7%
C ₁₀	2-7%
C ₁₂	45-55%
C ₁₄	15-25%
C ₁₆	4-14%
C ₁₈	4-14%

[0009] The biodegradable nonionic surfactant is a linear alkoxyated fatty acid or a linear unsaturated alkoxyated fatty alcohol. In the present application "alkoxyated" signifies that the compound is obtainable (although it may be obtained in alternative ways using alternative starting substances) from a reaction between a fatty acid or fatty alcohol and an alkylene oxide, such as for instance - but not restricted to - ethylene oxide or propylene oxide. In a preferred embodiment the alkoxyated unsaturated fatty alcohol is derived from unsaturated C₁₀ - C₂₀ alcohols containing one or two double bonds. The unsaturation has a positive impact on the wettability of the treated cellulosic material. In a particularly preferred embodiment the alkoxyated unsaturated fatty alcohol is etoxyated oleyl cetylalcohol obtainable from an addition reaction between ethylene oxide and oleyl cetylalcohol in a molar relation of up to about 15 moles of ethylene oxide to about 1 mole of oleyl cetylalcohol, preferably between about 4-6 moles of ethylene oxide to about 1 mole of oleyl cetylalcohol. It is particularly preferred that the surfactant is obtainable from an addition reaction between 5 ethylene oxide and 1 mole of oleyl cetylalcohol. This preferred surfactant has Chemical Abstracts Service Registry Number 68155-01-1. Again, the term "obtainable" indicates that the etoxyated oleyl cetylalcohol may be obtained by alternative reaction routes.

[0010] Apart from the active substances discussed above the composition may contain various additives, for instance solution viscosity reducing additives such as suitable glycols, e.g. ethylene glycol or propylene glycol, ethanol, or the ethyl ether of diethylene glycol.

[0011] As indicated above the present invention also relates to a method for antistatic and softening treatment of cellulosic materials in which the present aqueous softening and antistatic agent composition is used. The cellulosic material may for instance be pulp, such as mechanical pulp (MP), stone groundwood pulp (SGW), pressure groundwood pulp (PGW), refiner mechanical pulp (RMP), thermo-mechanical pulp (TMP), chemi-mechanical pulp (CMP), or chemi-thermomechanical pulp (CTMP). In a preferred embodiment the cellulosic material is fluff pulp, i.e. pulp intended for dry shredding to yield fluff. The cellulosic material may also be fluff or tissue. The present method may be used for the production of a number of cellulosic products the softness of which is of great importance, such as toilet paper, hygienic tissues, tissue paper, paper sheets, paper fabrics, paper towels, paper tablecloths, and paper clothing.

[0012] At said treatment the present composition may be added to cellulose material suspended in water, for instance in the stock of a pulp production process prior to the forming of the pulp sheet. The amount of the present composition in the stock is suitably up to about 10 kg/ton of dry pulp, preferably up to about 5 kg/ton. Alternatively, the composition - optionally diluted with water to a concentration of about 2-5 grams per litre of water - may be sprayed on dry cellulosic material, e.g. on dry fluff pulp or dry tissue.

[0013] The present invention will now be illustrated by means of a non-limiting example.

Example : A composition according to the present invention was prepared, containing the substances set forth in Table II below, and in the respective percentages indicated therein.

Table II

benzyl-cocoalkyldimethyl-ammonium chloride	about 20 weight-%
oleyl cetylalcohol ethoxylated with 5 ethylene oxid units	about 75 weight-%
water	about 2.5 weight-%
propylene glycol	about 2.5 weight-%

[0014] A reference composition was also prepared, containing the substances set forth in Table III below, also in the percentages indicated therein.

Table II

benzyl-cocoalkyldimethyl-ammonium chloride	about 12.5 weight-%
water	about 87.5 weight-%

[0015] Both compositions were added to different samples of a 2% sulphate pulp slurry in amounts of 2 and 4 kg/ton dry pulp. Sheets were formed from the pulp slurries, and after drying the sheets were tested with respect to softness (the burst factor, measured according to SCAN-P 24:77 and indicated as percent of a blank test, and the tear energy in kJ/kg); and to the static potential in kV.

[0016] The obtained results are set forth in Table IV below.

Table IV

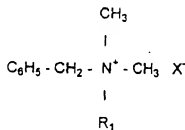
	Kg composition per ton of dry pulp	Reference composi- tion	Composition accord- ing to the invention
Burst factor	2	100	73
	4	100	41
Tear energy, kJ/kg	0	160	160
	2	156	119
	4	160	69
Static potential, kV	0	10	10
	2	1	4
	4	-2	0

[0017] The tear energy and the static potential were measured by means of method in which conditioned pulp sheets are cut into 30 x 210 mm strips, weighed, and placed in the feeding chute of Laboratory Pin Fibrizer (sold by Stora Kopparberg, Corporate Research Center, Falun, Sweden), equipped with an electronic display indicating the energy required for the fibrillation of the sheet, and the main and the feeding motors are started. A predetermined length of the strip is defibred by the rotating fibrizer's pin cylinder, after which the feeding motor is reversed to remove the undefibred part of the sheet. The remaining part of the sheet is weighed, and from this the defibred amount of sheet may be derived. The ratio between the energy reading on the display and said defibred amount is the tear energy, measured in kJ/kg. An electrostatic voltmeter (JCI 148 from John Chubb Instrumentation) is used to measure the static potential of the defibred amount of sheet.

[0018] As can be seen the present composition has, in contrast to the reference composition, a clear effect with regard to all of the parameters listed in Table IV, in particular a clearly improved impact on the softness parameters.

Claims

1. An aqueous softening and antistatic agent composition comprising a quaternary ammonium compound and a biodegradable nonionic surfactant, **characterised** in that the composition comprises a quaternary ammonium compound having the formula



wherein R_1 a $\text{C}_6 - \text{C}_{22}$ hydrocarbyl group; and X is halogen or SO_4^{2-} , in a concentration of at least about 15% by weight, and in that the surfactant is a linear unsaturated fatty acid or a linear alkoxyated unsaturated fatty alcohol.

2. The composition according to claim 1, **characterised** in that the quaternary ammonium compound is a benzyl-cocoalkyldimethyl-ammonium salt.
3. The composition according to claim 1, **characterised** in that the concentration of said salt is at least about 20% by weight.
4. The composition according to claim 1, **characterised** in that said biodegradable nonionic surfactant is an alkoxyated oleyl cetylalcohol.
5. The composition according to claim 1, **characterised** in that said biodegradable nonionic surfactant is an etoxyated oleyl cetylalcohol.
6. The composition according to claim 5, **characterised** in that said etoxyated oleyl cetylalcohol is obtainable by reacting ethylene oxid with oleyl cetylalcohol in a molar relation of up to about 15 moles of ethylene oxid to about 1 mole of oleyl cetylalcohol.
7. The composition according to claim 6, **characterised** in that the molar relation is between about 4-6 moles of ethylene oxid to about 1 mole of oleyl cetylalcohol.
8. A method for providing cellulosic materials with a reduced tendency to retain an electrostatic charge as well as providing the material with improved softness, **characterised** in that the cellulosic material is treated with a composition according to any of the preceding claims.
9. Fluff obtainable from fluff pulp that has been treated with a composition according to any one of claims 1-7.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 20 1485

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 6)
X	DE 14 69 405 A (IMPERIAL CHEMICAL INDUSTRIES LTD.) 12 December 1968 * page 3, paragraph 3 - page 6, paragraph 4; claim 1; examples *	1-9	C09K3/16 D21C9/00 D21H17/72 //D21H17:06, 17:07,17:14
Y	DE 35 36 258 A (COLGATE PALMOLIVE CO) 17 April 1986 * page 14, line 1 - page 15, line 20 * * page 16, line 1 - page 18, line 9 * * claims *	1-8	
Y	US 4 351 699 A (OSBORN III THOMAS W) 28 September 1982 * column 2, line 13 - line 36 * * column 3, line 14 - line 43 * * column 4, line 18 - column 5, line 31 *	1-9	
Y	US 4 441 962 A (OSBORN III THOMAS W) 10 April 1984 * column 3, line 21 - line 48 * * column 4, line 47 - column 5, line 37; claims *	1-9	TECHNICAL FIELDS SEARCHED (Int. Cl. 6)
X	DE 29 29 512 A (KENOGARD AB) 31 January 1980 * page 3, paragraph 2 - page 7, paragraph 2 * * page 8, paragraph 3; claims *	1-9	C09K D21C D21H
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 14 August 1998	Examiner Koegler-Hoffmann, S
CATEGORY OF CITED DOCUMENTS			
<p>X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document</p> <p>T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &: member of the same patent family, corresponding document</p>			

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 98 20 1485

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

14-08-1998

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 1469405 A	12-12-1968	BE 660859 A	09-09-1965
		FR 1430557 A	20-05-1966
		GB 1069369 A	
		GB 1107372 A	
DE 3536258 A	17-04-1986	AT 394377 B	25-03-1992
		AU 578748 B	03-11-1988
		AU 4875885 A	24-04-1986
		BE 903464 A	17-04-1986
		CH 669960 A	28-04-1989
		DK 476085 A	18-04-1986
		FI 854032 A	18-04-1986
		FR 2571736 A	18-04-1986
		GB 2168374 A, B	18-06-1986
		JP 61097396 A	15-05-1986
		LU 86126 A	11-06-1986
		NL 8502839 A	16-05-1986
		PT 81315 B	24-03-1987
		SE 8504661 A	18-04-1986
		US 4790856 A	13-12-1988
US 4351699 A	28-09-1982	AU 7633481 A	22-04-1982
		EP 0049924 A	21-04-1982
		JP 57136426 A	23-08-1982
		US 4441962 A	10-04-1984
US 4441962 A	10-04-1984	US 4351699 A	28-09-1982
		AU 7633481 A	22-04-1982
		EP 0049924 A	21-04-1982
		JP 57136426 A	23-08-1982
DE 2929512 A	31-01-1980	SE 425512 B	04-10-1982
		CA 1129604 A	17-08-1982
		FI 792168 A, B,	22-01-1980
		FR 2431569 A	15-02-1980
		SE 7808056 A	23-01-1980
		US 4303471 A	01-12-1981

EPO FORM 1484

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82